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Form PTO-1390 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEYS DOCKET NUMBER RN99119	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN) NOT APPLICABLE 10/088455	
INTERNATIONAL APPLICATION NO. PCT/FR00/02704		INTERNATIONAL FILING DATE September 29, 2000		PRIORITY DATE CLAIMED September 29, 2000	
TITLE OF INVENTION PROCESS FOR PREPARING MIXED SUBSTITUTED ALKYNYL ETHERS					
APPLICANT (S) FOR DO/EO/US: Roland JACQUOT					
Applicant herewith submits the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371 (f)). The submission must include items (5), (6), (9) and 24 indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c) (2)) a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made, however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (SIGNED) 10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210)					
Items 13 to 18 below concern document(s) or information included:					
13. <input checked="" type="checkbox"/> An information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 16. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 17. <input type="checkbox"/> A substitute specification. 18. <input type="checkbox"/> A change of power of attorney and/or address letter 19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825. 20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 22. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail. 23. <input type="checkbox"/> Other items or information: <input checked="" type="checkbox"/> Form PCT/IB/332 <input checked="" type="checkbox"/> Form PCT/IB/308 <input checked="" type="checkbox"/> Form PCT/ISA/210 French version <input checked="" type="checkbox"/> Form PCT/ISA/210 English Version <input checked="" type="checkbox"/> Form PCT/IPEA/409 French Version <input type="checkbox"/> Form PCT/IPEA/409 Translation in English Language <input checked="" type="checkbox"/> Form PCT/IPEA/416 French version <input type="checkbox"/> Form PCT/IPEA/416 English Version <input checked="" type="checkbox"/> PCT/FR00/02704 as published <input type="checkbox"/> Form PCT/IB/306					

JC13 Rec'd PCT/PTO 13 MAR 2002

U.S. APPLICATION NO. (IF KNOWN) NOT APPLICABLE		INTERNATIONAL APPLICATION NO. PCT/ FR00/02704		ATTORNEYS DOCKET NUMBER RN99119	
24. The following fees are submitted:					CALCULATIONS PTO ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO					\$1,040.00
<input checked="" type="checkbox"/> International preliminary examination fee not paid to USPTO but International Search Report prepared by the EPO or JPO.....					\$890.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search (37 CFR 1.4445 (a)(2)) fee paid to USPTO.....					\$740.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4).....					\$710.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(2)-(4).....					\$100.00
ENTER APPROPRIATE BASIC FEE AMOUNT =					\$890.00
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30					\$0.00
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	30 - 20 =	10	X \$18.00		\$180.00
Independent Claims	1 - 3 =	0	X \$84.00		\$0.00
Multiple Dependent Claims (Check if applicable) <input type="checkbox"/>					\$0.00
TOTAL OF ABOVE CALCULATIONS =					\$1,070.00
<input type="checkbox"/> Applicant claims small entity status. (See 37 CFR 1.127). The fees indicated above are reduced by 1/2.					\$0.00
SUBTOTAL =					\$1,070.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).					\$0.00
TOTAL NATIONAL FEE =					\$0.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable) <input checked="" type="checkbox"/>					\$40.00
TOTAL FEES ENSLOED =					\$1,110.00
					Amount to be:
					refunded
					charged
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 18-1171 in the amount of \$1,110.00 to cover the above fees. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 18-1171 . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDANCE TO Kevin E. McVEIGH RHODIA INC. 259 Prospect Plains Road CN 7500 CRANBURY, NJ 08512 TEL: (609) 860-4194					
 SIGNATURE Kevin McVEIGH NAME 33,017 REGISTRATION NUMBER MARCH 13, 2002 DATE					

Express Mail Label #: EL 822429972US

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Case RN99119

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Roland JACQUOT

National Phase of PCT/FR00/02704

International Filing Date : 09/29/2000

Serial No: To be assigned

Filing Date: To be assigned

**For: PROCESS FOR PREPARING MIXED SUBSTITUTED ALKYNYL
ETHERS**

Examiner: N/A

Art Unit: N/A

Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Prior to calculation of filing fee, please enter the following amendment in the
specification and claims:

In the Specification:

Page 1, just after the title, please add the new following paragraph:

This application is an application under 35 U.S.C. Section 371 of International
Application Number PCT/FR00/02704 filed on September 29, 2000.

In the Claims:

Please cancel claims 1 to 22, and replace them with the following new claims 23 to 52:

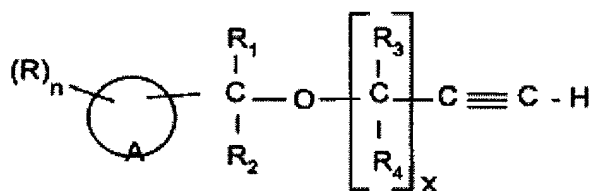
23. (New) A process for preparing a substituted mixed ether of benzyl/alkynyl type
from a starting mixed ether of benzyl/alkynyl type comprising a hydrogen atom on a
triple bond, said process comprising the steps of reacting a starting mixed ether of
benzyl/alkynyl type, derived from a benzyl type alcohol and an alkynyl alcohol,

- n is a number smaller than or equal to 5, and

- x is a number from 1 to 10.

25. (New) A process according to claim 24, wherein x is a number from 1 to 5.

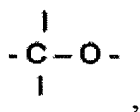
26. (New) A process according to claim 23, wherein in that the starting mixed ether of benzyl/alkynyl type has the following general formula (I):



(I)

wherein:

- A represents a residue of a cycle forming all or a part of an aromatic, monocyclic or polycyclic, carbocyclic or heterocyclic system comprising at least one group of formula:



- R represents one or more substituent(s), which are identical or different,

- R₁ and R₂, which are identical or different, represent:

- a linear or branched, saturated or unsaturated, acyclic alkyl group, having an hydrocarbon chain, comprising 1 to 6 carbon atoms, the hydrocarbon chain being optionally interrupted by a heteroatom, or a functional group, and carrying optionally substituents,

- a linear or branched, saturated or unsaturated, acyclic aliphatic group carrying a cyclic substituent, being optionally substituted, said acyclic group being connected to the cycle via a covalent bond, a heteroatom or a functional group,
 - a carbocyclic group, saturated or comprising 1 or 2 unsaturated bonds in the cycle, containing 3 to 8 carbon atoms in the cycle, said cycle being optionally substituted,
 - an aromatic monocyclic carbocyclic group, containing at least 4 carbon atoms in the cycle, said cycle being optionally substituted, or
 - a CF₃ group, for one of groups R₁ and R₂.
- R₃ and R₄, which are identical or different, represent a hydrogen atom or a hydrocarbon group containing 1 to 12 carbon atoms,
- n is a number smaller than or equal to 5, and
- x is a number from 1 to 10.

27. (New) A process according to claim 24, wherein A is a residue of a cyclic compound comprising at least 4 carbon atoms in the cycle, optionally substituted, and representing at least one of the following cycles:

- an aromatic, monocyclic or polycyclic carbocycle, or
- an aromatic, monocyclic or polycyclic heterocycle comprising at least one heteroatom selected from the group consisting of O, N or S.

28. (New) A process according to claim 27, wherein A is a residue of a benzene or naphthalene cycle, optionally substituted.

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29. (New) A process according to claim 27, wherein A carry one or more electron-donating group(s) selected from the group consisting of:

- linear or branched alkyl groups,
- linear or branched alkenyl groups,
- linear or branched halogenoalkyl groups,
- cycloalkyl groups comprising 3 to 6 carbon atoms,
- a phenyl group,
- alkoxy groups of formula R_5-O- or thioether groups of formula R_5-S- , wherein R_5 represents a linear or branched alkyl group comprising 1 to 6 carbon atoms, or a phenyl group,
- groups of formula $-N-(R_6)_2$, wherein R_6 groups, which are identical or different, represent a hydrogen atom, a linear or branched alkyl group comprising 1 to 6 carbon atoms, or a phenyl group, and
- a $-CF_3$ group.

30. (New) A process according to claim 27, wherein A carry one or more electron-donating group(s) selected from the group consisting of:

- linear or branched alkyl groups, comprising 1 to 4 carbon atoms,
- linear or branched alkenyl groups, comprising 2 to 4 carbon atoms,
- linear or branched halogenoalkyl groups, comprising 1 to 4 carbon atoms,
- a cyclohexyl group,
- a phenyl group,

- alkoxy groups of formula R_5-O- or thioether groups of formula R_5-S- , wherein R_5 represents a linear or branched alkyl group comprising 1 to 4 carbon atoms, or a phenyl group,
- groups of formula $-N(R_6)_2$, wherein R_6 groups, which are identical or different, represent a hydrogen atom, a linear or branched alkyl group comprising 1 to 4 carbon atoms, or a phenyl group, and
- a $-CF_3$ group.

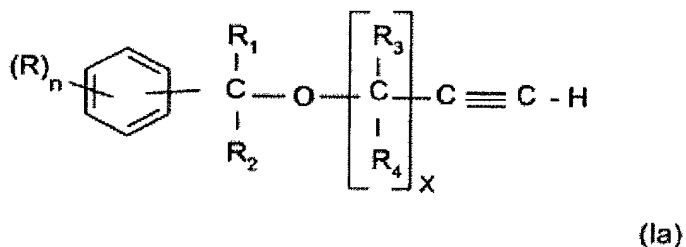
31. (New) A process according to claim 24, wherein n is greater than or equal to 2, two groups R and 2 successive atoms on the aromatic cycle being bonded together via an alkylene, alkenylene or alkenylidene group containing 2 to 4 carbon atoms, to form a saturated, unsaturated or aromatic heterocycle containing 5 to 7 carbon atoms, one or more carbon atoms being optionally replaced by a further heteroatom.

32. (New) A process according to claim 24, wherein n is greater than or equal to 2, two groups R and 2 successive atoms on the aromatic cycle being bonded together via an alkylene, alkenylene or alkenylidene group containing 2 to 4 carbon atoms, to form a saturated, unsaturated or aromatic heterocycle containing 5 to 7 carbon atoms, one or more carbon atoms being optionally replaced by a further oxygen atom.

33. (New) A process according to claim 24, wherein R₃ and R₄, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 12 carbon atoms.

34. (New) A process according to claim 33, wherein R₃ and R₄, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

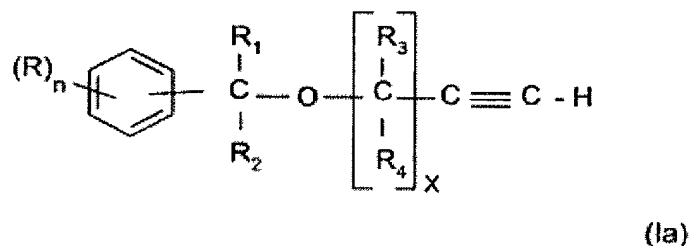
35. (New) A process according to claim 23, wherein that the starting mixed ether of benzyl/alkynyl type has the following general formula (Ia):



wherein:

- n is a number equal to or smaller than 4,
- x is a number equal to 1, 2 or 3,
- R group or groups are electron-donating groups,
- R₁ and R₂ groups, which are identical or different, represent:
 - a hydrogen atom,
 - a linear or branched alkyl group containing 1 to 6 carbon atoms,
 - a cycloalkyl group containing 3 to 8 carbon atoms,
 - a phenyl group,
 - a phenylalkyl group containing 7 to 12 carbon atoms, or
 - a CF₃ group, and
- R₃ and R₄ groups, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

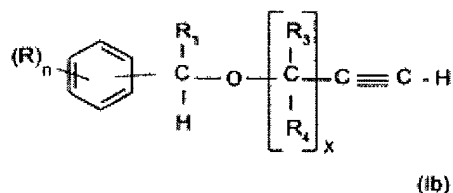
36. (New) A process according to claim 23, wherein that the starting mixed ether of benzyl/alkynyl type has the following general formula (Ia):



wherein:

- n is 1 or 2,
- x is a number equal to 1, 2 or 3,
- R group or groups are methylenedioxy or ethylenedioxy groups,
- R₁ and R₂ groups, which are identical or different, represent:
 - a hydrogen atom,
 - a methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl group,
 - a cyclopentyl or cyclohexyl group,
 - a phenyl group,
 - a benzyl group, or
 - a CF₃ group, and
- R₃ and R₄ groups, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

37. (New) A process according to claim 23, wherein the starting mixed ether of benzyl/alkynyl type has the following formula (Ib):



wherein:

- n is equal to 1 or 2,
- R group or groups represent an alkyl or alkoxy group containing 1 to 4 carbon atoms, or a methylenedioxy group, and
- R₁ represents a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

38. (New) A process according to claim 23, wherein the starting mixed ether of benzyl/alkynyl type is [1-(prop-1-ynyloxy)ethyl]-3,4 dimethoxybenzene.

39. (New) A process according claim 23, wherein the alkylation agent is a dialkylsulphate or a halide compound.

40. (New) A process according to claim 39, wherein the alkylation agent is a dialkylsulphate having the following formula (IVa):



wherein R₇ represents a linear or branched alkyl group containing 1 to 6 carbon atoms.

41. (New) A process according to claim 39, wherein the alkylation agent is a halide compound having the following formula (IVb):



wherein:

- R_8 represents a linear or branched, saturated or unsaturated, acyclic aliphatic hydrocarbon group containing 1 to 20 carbon atoms, a saturated, unsaturated or aromatic, monocyclic or polycyclic, cycloaliphatic group, or a linear or branched, saturated or unsaturated aliphatic group carrying a cyclic substituent, and
- X represents a bromine, chlorine or iodine atom.

42. (New) A process according to claim 41, wherein X represents a chlorine atom or an iodine atom and R_8 represents a linear or branched alkyl group containing 1 to 4 carbon atoms.

43. (New) A process according to claim 39, wherein the alkylation agent is dimethylsulphate, methyl iodide, methyl chloride, chloroethane, methyl bromide or bromoethane.

44. (New) A process according to claim 23, wherein the anionisation agent is an amide base, a metallic alcoholate or an alkali metal.

45. (New) A process according to claim 44, wherein the anionisation agent is selected from the group consisting of lithium diisopropylamide, lithium hexamethyldisilazane, prepared or used in situ by the action of a strong lithiated base on a corresponding amine, alkali metal alcoholates, sodium, and potassium.

46. (New) A process according to claim 45, wherein the alkali metal alcoholate is sodium or potassium methylate, ethylate or tert-butate.

47. (New) A process according to claim 45, wherein the anionisation agent is sodium or potassium amide.

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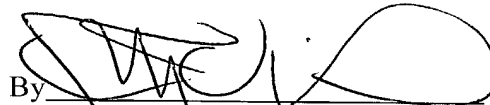
REMARKS

The preliminary amendments are filed to comply with the claims structure and wording according to the United States Patent law. It is asserted that these amendments do not add new matter. Support for these amendments can be found in the specification and claims as originally filed. Entry of these amendments is respectfully requested.

March 13, 2002

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Respectfully submitted,

By 

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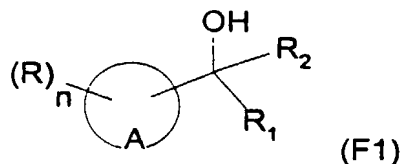
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PROCESS FOR PREPARING MIXED SUBSTITUTED ALKYNYL ETHERS

The present invention relates to a process for preparing mixed substituted alkynyl ethers. More particularly, the invention relates to the preparation of mixed ethers derived from a benzyl type alcohol and a substituted alkynyl alcohol.

International patent application PCT/FR98/01472 describes a process for etherifying a benzyl type alcohol that consists of reacting said alcohol with a further alcohol, in the presence of a catalyst, said process being characterized in that the etherification reaction is carried out in the presence of an effective quantity of a zeolite.

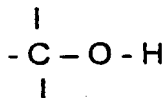
The benzyl type alcohol employed has the following general formula:



in which:

- A represents the residue of a cycle forming all or part of an aromatic, monocyclic or polycyclic, carbocyclic or heterocyclic system;
- R represents one or more substituents that may be identical or different;
- R₁ and R₂, which may be identical or different, represent a hydrogen atom, a functional group or a hydrocarbon group containing 1 to 24 carbon atoms;
- n is a number equal to 5 or less.

The term "benzyl type alcohol" as used in the description of the present invention means not only an aromatic carbocycle but also an aromatic heterocycle wherein one hydrogen atom directly bonded to the aromatic ring is replaced by a group:



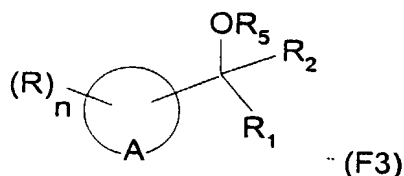
and the term "aromatic" means the conventional notion of aromaticity as defined in the literature, in particular by Jerry MARCH, "Advanced Organic Chemistry", 4th edition, John Wiley and Sons, 1992, pp. 40 ff.

The alcohol caused to react has the following formula:



in which R_5 represents a hydrocarbon group containing 1 to 24 carbon atoms, which can be a linear or branched, saturated or unsaturated, acyclic aliphatic group; a saturated, unsaturated or aromatic cycloaliphatic group; or a linear or branched, saturated or unsaturated aliphatic group, carrying a cyclic substituent.

The ether of the benzyl type alcohol with formula (F1) and the alcohol with formula (F2) obtained can be symbolised by formula (F3):



in which:

- A, n, R, R_1 , R_2 and R_5 have the meanings given above.

Alcohols with formula (F2) that can be used include unsaturated alcohols such as substituted alkynyl alcohols, in particular 2-butyne-1-ol represented by the formula



The disadvantage of using such a substituted alkynyl alcohol resides in its very high cost compared with the propargylic alcohol with formula $H - C \equiv C - CH_2 - OH$.

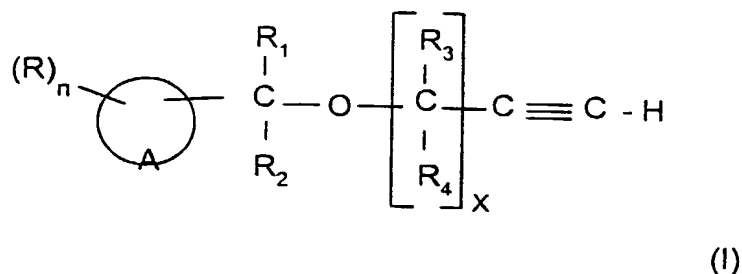
The aim of the present invention is to provide a cheap process for preparing an ether derived from a benzyl type alcohol and a substituted alkynyl alcohol, i.e., in which the hydrogen atom of the alkyne function has been substituted by a hydrocarbon group.

It has now been discovered, and this constitutes the subject matter of the present invention, a process for preparing a mixed ether of the benzyl/substituted alkynyl type from a

mixed ether of the benzyl/alkynyl-type with a hydrogen atom on the triple bond, characterized in that it consists of reacting a mixed ether derived from a benzyl type alcohol and an alkynyl alcohol carrying a hydrogen atom on the triple bond with an alkylation agent, in the presence of an anionisation agent.

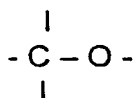
In accordance with the process of the invention, the starting substance is a true alkynyl mixed ether, i.e., the alkyne function carries a hydrogen atom.

More precisely, we start from an ether derived from a benzyl type alcohol and an alkynyl alcohol, with general formula (I):



in which:

- A represents the residue of a cycle forming all or part of an aromatic, monocyclic or polycyclic, carbocyclic or heterocyclic system comprising at least one group



- R represents one or more substituents which may be identical or different;
- R₁ and R₂, which may be identical or different, represent a hydrogen atom, a functional group or a hydrocarbon group containing 1 to 24 carbon atoms, which can be a linear or branched, saturated or unsaturated acyclic aliphatic group; a saturated, unsaturated or aromatic, monocyclic or polycyclic cycloaliphatic group; or a linear or branched, saturated or unsaturated aliphatic group carrying a cyclic substituent;
- R₃ and R₄, which may be identical or different, represent a hydrogen atom or a hydrocarbon group containing 1 to 12 carbon atoms;

- n is a number equal to 5 or less;
- x is a number from 1 to 10, preferably 1 to 5.

The mixed alkynyl ether involved in the process of the invention satisfies formula (I) in which R_1 and R_2 represent a linear or branched, saturated or unsaturated, acyclic aliphatic group.

More preferably, R_1 and R_2 represent a linear or branched alkyl group containing 1 to 12 carbon atoms, preferably 1 to 6 carbon atoms; the hydrocarbon chain can optionally be interrupted by a heteroatom (for example oxygen), by a functional group (for example $-\text{CO}-$) and/or may carry a substituent (for example a halogen).

The linear or branched, saturated or unsaturated, acyclic aliphatic group can optionally carry a cyclic substituent. The term "cycle" preferably means a saturated, unsaturated or aromatic, carbocyclic or heterocyclic cycle, preferably cycloaliphatic or aromatic, in particular cycloaliphatic comprising 6 carbon atoms in the cycle, or a benzene ring. The aliphatic acyclic group can be connected to the cycle by a covalent bond, a heteroatom or a functional group; examples are given below.

The cycle can optionally be substituted; possible examples of cyclic substituents are substituents such as R, the meaning of which has been defined above.

R_1 and R_2 can also represent a saturated carbocyclic group or a carbocyclic group comprising 1 or 2 unsaturated bonds in the cycle, generally containing 3 to 8 carbon atoms, preferably 6 carbon atoms in the cycle; said cycle can be substituted by substituents such as R.

R_1 and R_2 can also represent an aromatic carbocyclic group, preferably monocyclic, generally containing at least 4 carbon atoms, preferably 6 carbon atoms in the cycle; said cycle may be substituted by substituents such as R.

One of groups R_1 and R_2 can represent a group CF_3 .

The invention is of particular application to mixed alkynyl ethers with formula (I) in which A is the residue of a cyclic compound preferably containing at least 4 carbon atoms in the

cycle, more preferably 5 or 6, optionally substituted, and representing at least one of the following cycles:

- an aromatic, monocyclic or polycyclic carbocycle;
- an aromatic, monocyclic or polycyclic heterocycle comprising at least one of heteroatoms O, N or S.

Without in any way limiting the scope of the invention, optionally substituted residue A can represent the residue:

- of an aromatic carbocyclic monocyclic compound such as benzene or toluene;
- of an aromatic condensed polycyclic compound such as naphthalene;
- or an aromatic, heterocyclic, monocyclic compound such as pyridine, furan or thiophene.

In the process of the invention, a mixed alkynyl ether with formula (I) is preferably used wherein A represents a benzene or naphthalene nucleus.

Residue A of the mixed alkynyl ether with formula (I) can carry one or more substituents provided that they do not react with the anionisation agent.

The number of substituents present on the cycle depends on the carbon condensation of the cycle and on the presence or otherwise of unsaturated bonds on the cycle.

The maximum number of substituents that are capable of being carried by a cycle can readily be determined by the skilled person.

Examples of substituents are given below, but this list is not limiting in any way. The following can be cited in particular:

- linear or branched alkyl groups, preferably containing 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms;
- linear or branched alkenyl groups, preferably containing 2 to 6 carbon atoms, more preferably 2 to 4 carbon atoms;

- linear or branched halogenoalkyl groups, preferably containing 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms;
- cycloalkyl groups containing 3 to 6 carbon atoms, preferably the cyclohexyl group;
- the phenyl group;
- alkoxy $R_5\text{-O-}$ or thioether $R_5\text{-S-}$ groups, in which R_5 represents a linear or branched alkyl group containing 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms or a phenyl group;
- $\text{-N(R}_6)_2$ groups, in which R_6 groups, which may be identical or different, represent a hydrogen atom, a linear or branched alkyl group containing 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, or a phenyl group;
- the group CF_3 .

When n is 2 or more, two groups R and the 2 successive atoms on the aromatic cycle can be bonded together via an alkylene, alkenylene or alkenylidene group containing 2 to 4 carbon atoms to form a saturated, unsaturated or aromatic heterocycle containing 5 to 7 carbon atoms. One or more carbon atoms may be replaced by a further heteroatom, preferably oxygen. Groups R can represent a methylenedioxy or ethylenedioxy group.

Preferred substituents are selected from electron-donating groups. The term "electron-donating group" means a group as defined by H. C. BROWN in the work by Jerry MARCH, "Advanced Organic Chemistry", Chapter 9, pages 243 and 244 (1985).

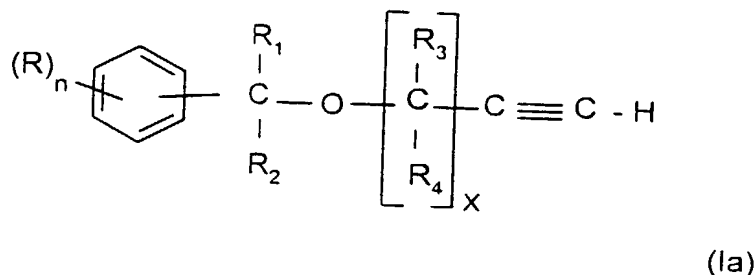
Regarding the meanings of R_3 and R_4 in formula (I), they more particularly represent a hydrogen atom or a linear or branched alkyl group containing 1 to 12 carbon atoms, preferably 1 to 4.

Preferred groups that can be mentioned for R_3 and R_4 are a hydrogen atom, a methyl, ethyl, propyl or isopropyl group.

Preferably, R_3 and R_4 represent a hydrogen atom.

In formula (I), x is a number equal to 1, 2 or 3.

More particularly, the process of the invention is applicable to mixed alkynyl ethers with formula (Ia):



in which:

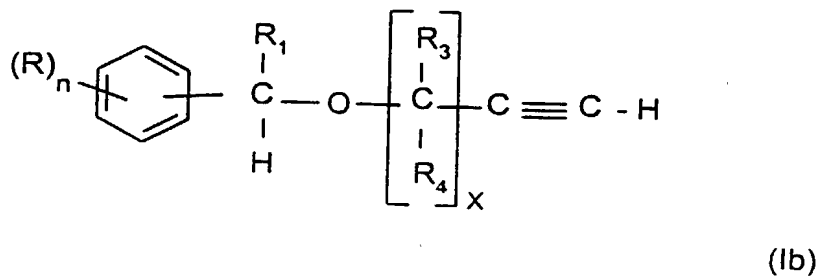
- n is a number equal to 4 or less, preferably 1 or 2;
- x is a number equal to 1, 2 or 3;
- group or groups R are electron-donating groups, preferably an alkyl or alkoxy group containing 1 to 4 carbon atoms, or methylenedioxy or ethylenedioxy;
- groups R₁ or R₂, which may be identical or different, represent:
 - a hydrogen atom;
 - a linear or branched alkyl group containing 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl;
 - a cycloalkyl group containing 3 to 8 carbon atoms, preferably a cyclopentyl or cyclohexyl group;
 - a phenyl group;
 - a phenylalkyl group containing 7 to 12 carbon atoms, preferably a benzyl group;
 - a CF₃ group;
- groups R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

Preferred compounds satisfy formula (Ia) in which:

- n is a number equal to 1 or 2;

- x is a number equal to 1, 2 or 3;
- groups R, which may be identical or different, represent an alkyl or alkoxy group containing 1 to 4 carbon atoms, or methylenedioxy or ethylenedioxy;
- groups R₁ and R₂, which may be identical or different, represent:
 - a hydrogen atom;
 - a linear or branched alkyl group containing 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl;
- groups R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

More particular compounds with formula (Ia) are mixed alkynyl ethers with formula (Ib):

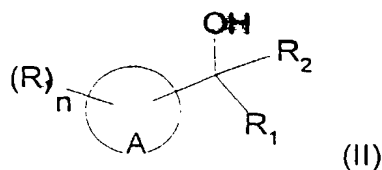


in which:

- n is equal to 1 or 2;
- group or groups R represent an alkyl or alkoxy group containing 1 to 4 carbon atoms, or methylenedioxy;
- group R₁ represents a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

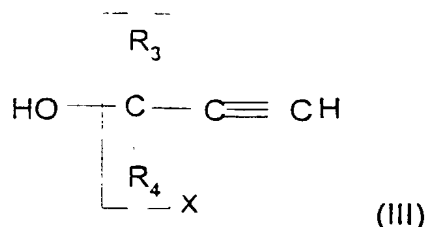
Compounds with formula (I) can be prepared as described in PCT/FR/98/01472 using a process that consists of reacting, in the presence of a zeolite:

- a benzyl type alcohol with formula:



in which formula, R, R₁, R₂, A and n have the meaning given above;

- and an unsaturated alcohol with formula:



in which formula R₃, R₄ and x have the meanings given above.

Compounds (II) and (III) are reacted in the presence of a zeolite.

Preferably, a zeolite is used such as:

- mordenite with a Si/Al mole ratio of 5 to 150, preferably 10 to 100, more preferably 10 to 25;
- β zeolites with a Si/Al mole ratio of more than 8, preferably in the range 10 to 100, more preferably in the range 12 to 50;
- Y zeolites with a Si/Al mole ratio in the range 2 to 50, preferably in the range 2 to 15.

The benzyl type alcohol with formula (II) can be reacted with the unsaturated alcohol with formula (III) in the presence or absence of an organic solvent, and one of the reactants can be used as the reaction solvent.

Non limiting examples of solvents that are suitable for use in the present invention that can be cited are aliphatic, cycloaliphatic or aromatic ether-oxides, more particularly diethyl oxide, dipropyl oxide, diisopropyl oxide, dibutyl oxide, methytertiobutylether, dipentyl oxide, diisopentyl oxide, phenyl oxide, benzyl oxide; dioxane, and tetrahydrofuran (THF).

When the process is carried out in batches, the catalyst can represent 2% to 50%, preferably 5% to 20% by weight with respect to the lowest quantity of reactant. However, if the process is carried out continuously, for example by reacting a mixture of benzyl type alcohol and unsaturated alcohol on a fixed catalyst bed, these catalyst/benzyl alcohol ratios have no significance and at a given time, there may be an excess weight of catalyst with respect to the starting benzyl alcohol.

The quantity of unsaturated alcohol with formula (III) expressed in moles of unsaturated alcohol per mole of benzyl type alcohol with formula (II) can also vary widely. The mole ratio of unsaturated alcohol with formula (III)/benzyl alcohol with formula (I) can be between 1 and 30. The upper limit is not critical but there is no advantage in exceeding it, for economic reasons.

The temperature of the etherification reaction can vary widely. It is advantageously in the range 50°C to 200°C, more preferably in the range 50°C to 100°C.

Generally, the reaction is carried out at atmospheric pressure, but higher pressures of 1 to 50 bars, preferably 1 to 25 bars, may also be suitable. Autogenous pressure conditions are used when the reaction temperature is higher than the boiling point of the reactants and/or products.

Preferably, the reaction is carried out in a controlled inert gas atmosphere, for example nitrogen or a rare gas such as argon.

The reaction period can vary widely. It is usually in the range 15 minutes to 10 hours, preferably in the range 30 minutes to 5 hours.

From a practical viewpoint, the process can be carried out continuously or in batches.

In a first variation, the catalyst, unsaturated alcohol with formula (III), and optional organic solvent can be charged then the benzyl type alcohol can be introduced. In a preferred implementation of the invention, the benzyl type alcohol is introduced progressively, either continuously or in aliquots, then the reaction mixture is heated to the desired temperature.

In a further variation of the invention, the reaction is carried out continuously in a tube reactor comprising the solid catalyst disposed in a fixed bed.

The benzyl type alcohol and the unsaturated alcohol are preferably introduced separately.

They can also be introduced into a solvent as mentioned above.

The residence time for the flow of material on the catalytic bed can be, for example, between 15 min and 10 hours, preferably in the range 30 min to 5 hours.

At the end of the reaction, a liquid phase is recovered comprising the etherified benzyl type alcohol with formula (I) which can be recovered conventionally.

In the process of the invention, C-alkylation of the compound with formula (I) obtained initially is carried out with the help of an alkylation agent. A first class of alkylation agents that can be used in the process of the invention is constituted by dialkylsulphates.

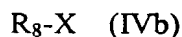
To this end, dialkylsulphates with the following formula are used:



in which R_7 represents a linear or branched alkyl group containing 1 to 6 carbon atoms.

Dimethylsulphate is preferred from the above alkylation agents.

A further suitable class is constituted by halide type compounds, in particular those represented by the following formula:



in which:

- R_8 represents a hydrocarbon group containing 1 to 20 carbon atoms, which can be a linear or branched, saturated or unsaturated, acyclic aliphatic group; a saturated, unsaturated or aromatic, monocyclic or polycyclic cycloaliphatic group; or a linear or branched, saturated or unsaturated aliphatic group carrying a cyclic substituent;
- X represents a bromine, chlorine or iodine atom.

The term "cycle" preferably means a saturated, unsaturated or aromatic carbocyclic or heterocyclic cycle, preferably cycloaliphatic or aromatic, in particular cycloaliphatic, containing 6 carbon atoms in the cycle, or a benzene ring.

Particularly suitable compounds with formula (IVb) are those in which R_8 represents a linear or branched C_1 to C_{10} alkyl group, a C_3 to C_{10} cycloalkyl group, a C_6 to C_{12} aryl group or a C_7 to C_{15} arylalkyl group, such as a benzyl group.

More preferably, it is a C_1 to C_{10} alkyl group; the alkyl chain may be interrupted by one or more oxygen atoms.

Preferred halides with formula (IVb) are those with formula (IVb) in which X is a chlorine or iodine atom and R_8 is a linear or branched alkyl group containing 1 to 4 carbon atoms.

More particularly, the following are employed: methyl iodide, methyl chloride, chloroethane, methyl bromide and bromoethane.

The quantity of alkylation agent used is equal to or greater than the stoichiometric quantity necessary to alkylate the hydrogen atom on the alkyne function.

Generally, the alkylation agent is employed in a quantity such that the ratio between the number of moles of alkylation agent and the number of hydrogen atoms replaced by an alkyl group R_9 (R_9 representing R_7 or R_8) is in the range 1 to 2, preferably in the range 1.1 to 1.3.

In accordance with the process of the invention, the mixed alkynyl ether with formula (I) and the alkylation agent are reacted in the presence of an agent for anionising the alkyne function to transform it into a $C\equiv C^-$ function.

Examples of reactants that can be cited in particular are amide type bases, metallic alcoholates and alkali metals.

An organic amide type base can be used, for example lithium diisopropylamide, lithium hexamethyldisilazane prepared or used in situ by the action of a strong lithiated base on the

corresponding amine but preferably, a mineral salt is used, preferably an alkali metal amide, more particularly sodium or potassium amide.

For economic reasons, sodium amide is used.

It is also possible to use an alkali metal alcoholate, preferably a sodium or potassium alcoholate, more preferably sodium or potassium methylate, ethylate or tert-butyrate.

It is also possible to use an alkali metal, preferably sodium or potassium.

The quantity of anionisation agent is at least equal to the stoichiometric quantity required, but it is generally employed in an excess of up to 20%.

The reaction is carried out in an organic solvent that is inert as regards the anionisation agent. Aliphatic or aromatic hydrocarbons can in particular be mentioned.

Examples of aliphatic hydrocarbons that can in particular be cited are paraffins such as hexane, heptane, octane, nonane, decane, undecane, dodecane, tetradecane or cyclohexane, and aromatic hydrocarbons, more particularly aromatic hydrocarbons such as benzene, toluene, xylenes, cumene and petroleum cuts constituted by a mixture of alkylbenzenes, particularly Solvesso® type cuts.

Toluene is preferred from the above list.

The quantity of organic solvent used can vary widely. It is such that the concentration by weight of the compound is advantageously in the range 5% to 50%, preferably in the range 20% to 30%.

The temperature at which the process of the invention is carried out is generally between 20°C and the reflux temperature of the reaction mixture, preferably between 50°C and 80°C.

The reaction pressure is selected by the skilled person as a function of the alkylation agent. It can be in the range 10^{-2} to 50 bars, preferably atmospheric pressure.

Preferably, the process of the invention is carried out in an inert gas atmosphere. A rare gas atmosphere can be employed, preferably argon, but nitrogen is cheaper.

From a practical viewpoint, the process of the invention is easy to carry out as no specific apparatus is required.

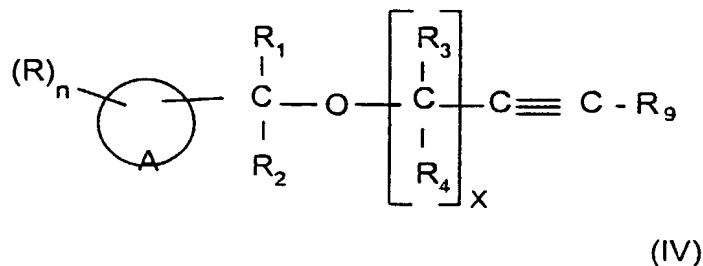
Practically, the process of the invention can be carried out as follows.

The various constituents of the reaction mixture are charged into the selected apparatus. The order of introduction is not critical. Preferably, the compound with formula (I) and the anionisation agent are brought into contact. The reaction medium is heated to the desired temperature, then the alkylation agent is added.

The desired product is recovered conventionally.

As an example, water can be added to re-dissolve the salts in an aqueous phase and an extraction solvent can be added, for example toluene.

The product obtained has formula (IV):



in which formula, the different symbols have the meanings given above.

Non limiting illustrative examples will now be given.

The terms TT and RR mean:

Degree of conversion (TT) = $\frac{\text{number of moles of reactant transformed}}{\text{Number of moles of reactant introduced}} \quad (\%)$

Yield (RR) = $\frac{\text{number of moles of alkynyl ether formed}}{\text{Number of moles of benzyl alcohol introduced}} \quad (\%)$

EXAMPLE 1

Preparation of [1-prop-1-ynyloxy]ethyl]-3,4 dimethoxybenzene

260 g of 1-[3,4-dimethoxyphenyl]-ethan-1-ol and 400 g of propargyl alcohol were introduced into a 1000 ml three-necked reactor.

It was stirred, and 40 g of HY zeolite with a Si/Al ratio of 2.7 was added.

It was slowly heated to 85°C.

It was maintained under these conditions for 2 hours.

It was cooled to 50°C and the catalyst was filtered off.

The excess propargyl alcohol was distilled off and recycled under reduced pressure.

Gas chromatographic analysis produced the following results:

TT: 100%; RR: 98%.

Preparation of [1-but-1-ynyloxy)ethyl]-3,4 dimethoxybenzene

100 ml of toluene was introduced into a 1000 ml reactor. It was stirred and the reactor was placed under a stream of nitrogen.

47 g of sodium amide was introduced.

With continuous stirring, a solution composed of 100 ml of toluene and 220 g of [1-prop-1-ynyloxy)ethyl]-3,4 dimethoxybenzene was added over 10 minutes.

It was heated to 80°C and kept under these conditions for 2 hours.

The reaction mixture was cooled to 20°C and 126 g of methyl sulphate was added over 15 min.

It was stirred for 1 hour at ambient temperature.

100 ml of water was added at ambient temperature.

It was decanted and the organic layer was washed with 100 ml of water.

It was concentrated and gas chromatographic analysis produced the following:

TT: 100%; RR: 98%.

EXAMPLE 2

Preparation of [1-but-1-ynyloxy)ethyl]-3,4 dimethoxybenzene

100 ml of toluene and 30 g of sodium were introduced into a 1000 ml reactor. It was stirred and the reactor was placed in a stream of nitrogen. It was heated to 120°C to melt the

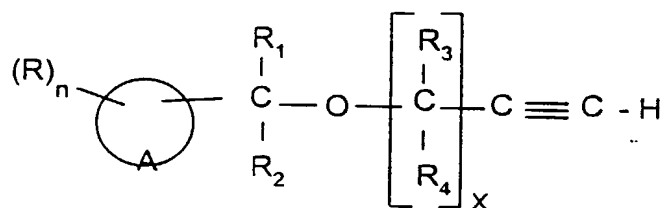
sodium and rapidly cooled to produce a dispersion of sodium. The preparation was continued as described in Example 1.

Gas chromatographic determination produced the following:

TT: 82%; RR: 56%.

CLAIMS

1. A process for preparing a mixed ether of the benzyl/substituted alkynyl type from a mixed ether of the benzyl/alkynyl type with a hydrogen atom on the triple bond, characterized in that it consists of reacting a mixed ether derived from a benzyl type alcohol and an alkynyl alcohol carrying a hydrogen atom on the triple bond with an alkylation agent, in the presence of an anionisation agent.
2. A process according to claim 1, characterized in that the mixed alkynyl ether has general formula (I):



(I)

in which:

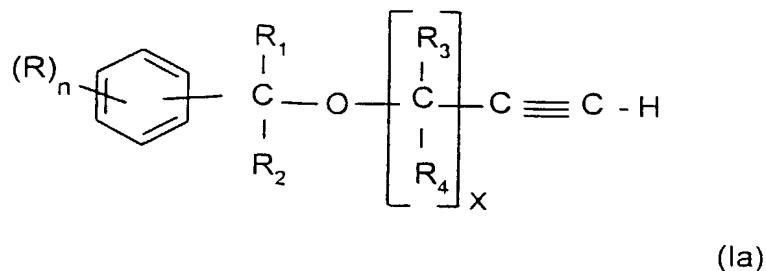
- A represents the residue of a cycle forming all or part of an aromatic, monocyclic or polycyclic, carbocyclic or heterocyclic system comprising at least one group

$$\begin{array}{c} | \\ \text{---} \text{C} \text{---} \text{O} \text{---} \\ | \end{array}$$
- R represents one or more substituents which may be identical or different;
- R₁ and R₂, which may be identical or different, represent a hydrogen atom, a functional group or a hydrocarbon group containing 1 to 24 carbon atoms, which can be a linear or branched, saturated or unsaturated, acyclic aliphatic group; a saturated, unsaturated or aromatic, monocyclic or polycyclic cycloaliphatic group; or a linear or branched, saturated or unsaturated aliphatic group carrying a cyclic substituent;
- R₃ and R₄, which may be identical or different, represent a hydrogen atom or a hydrocarbon group containing 1 to 12 carbon atoms;
- n is a number equal to 5 or less;
- x is a number from 1 to 10, preferably 1 to 5.

3. A process according to claim 1 or claim 2, characterized in that the mixed alkynyl ether has general formula (I) in which R_1 and R_2 , which may be identical or different, represent:
- a linear or branched, saturated or unsaturated, acyclic aliphatic group, preferably a linear or branched alkyl group containing 1 to 12 carbon atoms, preferably 1 to 6 carbon atoms; the hydrocarbon chain is optionally interrupted by a heteroatom, a functional group and/or it may carry substituents;
 - a linear or branched, saturated or unsaturated, acyclic aliphatic group carrying a cyclic substituent that may be substituted: said acyclic group can be connected to the cycle via a covalent bond, a heteroatom or a functional group;
 - a carbocyclic group that is saturated or comprises 1 or 2 unsaturated bonds in the cycle, generally containing 3 to 8 carbon atoms, preferably 6 carbon atoms in the cycle; said cycle may be substituted;
 - an aromatic carbocyclic group, preferably monocyclic, generally containing at least 4 carbon atoms, preferably 6 carbon atoms in the cycle; said cycle may be substituted;
- and one of groups R_1 and R_2 can represent a CF_3 group.
4. A process according to any one of claims 1 to 3, characterized in that the mixed alkynyl ether has general formula (I) in which residue A is the residue of a cyclic compound preferably containing at least 4 carbon atoms in the cycle, more preferably 5 or 6, optionally substituted, and representing at least one of the following cycles:
- an aromatic, monocyclic or polycyclic carbocycle, preferably a benzene ring or a naphthalene cycle;
 - an aromatic, monocyclic or polycyclic heterocycle comprising at least one of heteroatoms O, N or S.
5. A process according to claim 4, characterized in that the mixed alkynyl ether has general formula (I) in which residue A can carry one or more electron-donating groups such as:

- linear or branched alkyl groups, preferably containing 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms;
 - linear or branched alkenyl groups, preferably containing 2 to 6 carbon atoms, more preferably 2 to 4 carbon atoms;
 - linear or branched halogenoalkyl groups, preferably containing 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms;
 - cycloalkyl groups containing 3 to 6 carbon atoms, preferably the cyclohexyl group;
 - the phenyl group;
 - alkoxy R_5-O- or thioether R_5-S- groups, in which R_5 represents a linear or branched alkyl group containing 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms or a phenyl group;
 - $-N-(R_6)_2$ groups, in which groups R_6 , which may be identical or different, represent a hydrogen atom, a linear or branched alkyl group containing 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, or a phenyl group;
 - the group CF_3 .
6. A process according to any one of claims 1 to 5, characterized in that the mixed alkynyl ether has general formula (I), in which, when n is 2 or more, two groups R and the 2 successive atoms on the aromatic cycle can be bonded together via an alkylene, alkenylene or alkenylidene group containing 2 to 4 carbon atoms to form a saturated, unsaturated or aromatic heterocycle containing 5 to 7 carbon atoms; one or more carbon atoms can be replaced by a further heteroatom, preferably oxygen.
7. A process according to any one of claims 1 to 6, characterized in that the mixed alkynyl ether has formula (I) in which R_3 and R_4 , which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 12 carbon atoms, preferably 1 to 4.

8. A process according to claim 1, characterized in that the mixed alkynyl ether has formula (Ia):



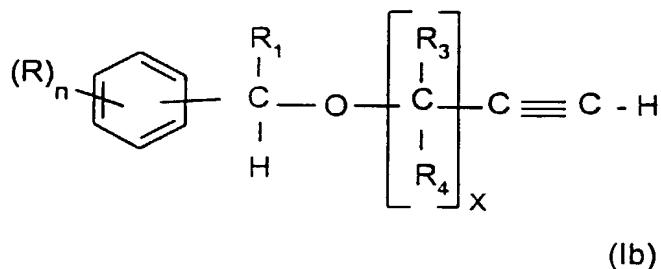
in which:

- n is a number equal to 4 or less, preferably 1 or 2;
- x is a number equal to 1, 2 or 3;
- group or groups R are electron-donating groups, preferably an alkyl or alkoxy group containing 1 to 4 carbon atoms, or methylenedioxy or ethylenedioxy;
- groups R₁ or R₂, which may be identical or different, represent:
 - a hydrogen atom;
 - a linear or branched alkyl group containing 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl;
 - a cycloalkyl group containing 3 to 8 carbon atoms, preferably a cyclopentyl or cyclohexyl group;
 - a phenyl group;
 - a phenylalkyl group containing 7 to 12 carbon atoms, preferably a benzyl group;
 - a CF₃ group;
- groups R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

9. A process according to claim 8, characterized in that the mixed alkynyl ether has formula (Ia) in which:

- n is a number equal to 1 or 2;
- x is a number equal to 1, 2 or 3;
- groups R, which may be identical or different, represent an alkyl or alkoxy group containing 1 to 4 carbon atoms or methylenedioxy or ethylenedioxy;
- groups R₁ and R₂, which may be identical or different, represent:
 - a hydrogen atom;
 - a linear or branched alkyl group containing 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl;
- groups R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

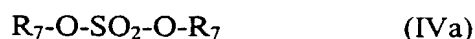
10. A process according to claim 1, characterized in that the mixed alkynyl ether has formula (Ib):



in which:

- n is equal to 1 or 2;
- group or groups R represent an alkyl or alkoxy group containing 1 to 4 carbon atoms, or methylenedioxy;
- group R₁ represents a hydrogen atom or a linear or branched alkyl group containing 1 to 4 carbon atoms.

11. A process according to claim 1, characterized in that the mixed alkynyl ether is [1-(prop-1-ynoxy)ethyl]-3,4 dimethoxybenzene.
12. A process according to any one of claims 1 to 11, characterized in that the alkylation agent is a dialkylsulphate or a halide type compound.
13. A process according to claim 12, characterized in that the alkylation agent is a dialkylsulphate with formula:



in which R_7 represents a linear or branched alkyl group containing 1 to 6 carbon atoms.

14. A process according to claim 12, characterized in that the alkylation agent is a halide type compound with formula:



in which:

- R_8 represents a hydrocarbon group containing 1 to 20 carbon atoms that can be a linear or branched, saturated or unsaturated, acyclic aliphatic group; a saturated unsaturated or aromatic, monocyclic or polycyclic cycloaliphatic group; or a linear or branched, saturated or unsaturated aliphatic group carrying a cyclic substituent;
 - X represents a bromine, chlorine or iodine atom.
15. A process according to claim 14, characterized in that the alkylation agent has formula (IVb) in which X is a chlorine atom or an iodine atom and R_8 is a linear or branched alkyl group containing 1 to 4 carbon atoms.
 16. A process according to claim 12, characterized in that the alkylation agent is dimethylsulphate, methyl iodide, methyl chloride, chloroethane, methyl bromide or bromoethane.
 17. A process according to any one of claims 1 to 16, characterized in that the anionisation agent is an amide type base, a metallic alcoholate or an alkali metal.

18. A process according to claim 17, characterized in that the anionisation agent is selected from: lithium diisopropylamide, lithium hexamethyldisilazane prepared or used in situ by the action of a strong lithiated base on the corresponding amine; an alkali metal alcoholate, preferably a sodium or potassium alcoholate, preferably sodium or potassium methylate, ethylate or tert-butyrate; and sodium or potassium.
19. A process according to claim 17 or claim 18, characterized in that the anionisation agent is sodium or potassium amide.
20. A process according to any one of claims 1 to 19, characterized in that the reaction is carried out in an organic solvent that is inert towards the anionisation agent, preferably an aliphatic or aromatic hydrocarbon.
21. A process according to any one of claims 1 to 20, characterized in that the temperature of the C-alkylation reaction is generally selected to be between 20°C and the reflux temperature of the reaction mixture, preferably between 50°C and 80°C.
22. A process according to any one of claims 1 to 21, characterized in that the compound with formula (I) and the anionisation agent are brought into contact; the reaction medium is heated to the desired temperature; the alkylation agent is added, and the substituted mixed alkynyl ether is recovered.

ABSTRACT OF THE DISCLOSURE

PROCESS FOR PREPARING MIXED SUBSTITUTED ALKYNYL ETHERS

The present invention relates to a process for preparing mixed substituted alkynyl ethers.

10 More particularly, the invention concerns the preparation of mixed ethers derived from a benzyl type alcohol and a substituted alkynyl alcohol. The process of the invention for preparing a benzyl/substituted alkynyl type mixed ether is prepared from a benzyl/alkynyl type mixed ether with a hydrogen atom on the triple bond is characterized in that it consists of reacting a mixed ether derived from a benzyl type alcohol and an alkynyl alcohol with a hydrogen atom on the
15 triple bond with an alkylation agent, in the presence of an anionisation agent.

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (include Reference to PCT International Applications) PCT/FR00/02704	ATTORNEY'S DOCKET NO RN99119
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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS FOR PREPARING MIXED SUBSTITUTED ALKYNYL ETHERS

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. _____

on _____

and was amended

on _____ (if applicable)

☒ was filed as PCT international application

Number **PCT/FR00/02704**

on **September 29, 2000,**

and amended under PCT ARTICLE 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations. §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY PCT indicate PCT	APPLICATION NUMBER	DATE OF FILING (day month year)	PRIORITY CLAIMED UNDER 35 USC 119	
FRANCE	99/12146	29 September , 1999	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Continued) (include Reference to PCT International Applications) PCT/FR00/02704				ATTORNEY'S DOCKET NO RN99119	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	US SERIAL NUMBERS ASSIGNED (if any)			
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney's and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number) JOHN A. SHEDDEN - Reg. No. 25,644, JOHN D. WOOD - Reg. No. 31,146 Kevin McVEIGH - Reg. No. 33,017					
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203	
<i>Roland Jacquot</i>					
DATE		DATE		DATE	
20 February 2002					